EFFICIENCY OF MANIPULATING DOSAGE OF FENTON'S REAGENTS EFFECTS TOWARDS THE DEGRADATION OF SULFINOL-D IN WASTEWATER

NOOR ZAHIDAH BINTI KHALID

CHEMICAL ENGINEERING
UNIVERSITI TEKNOLOGI PETRONAS
JULY 2009

Efficiency of Manipulating Dosage of Fenton's Reagents Effects Towards the Degradation of Sulfinol-D in Wastewater

by

Noor Zahidah binti Khalid

7469

A project dissertation submitted in partial fulfilment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

JULY 2009

Universiti Teknologi PETRONAS

Bandar Seri Iskandar

31750 Tronoh

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Efficiency of Manipulating Dosage of Fenton's Reagents Effects Towards the Degradation of Sulfinol-D in Wastewater

by

Noor Zahidah binti Khalid

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

(Assoc. Prof. Ir. Abdul Aziz Omar)

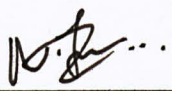
UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

July 2009

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.



NOOR ZAHIDAH BINTI KHALID

ABSTRACT

Amine based absorbents are frequently used for gas sweetening process. Waste water containing these absorbents are characterized of having high chemical oxygen demand (COD) in the range of 5000 to 25000 mg/L such waste water is difficult to treat by the conventional biological process. Several options has been identified to reduce the organic loading as well as to completely render the waste water to harmless effluent. One of the treatments is to use the Fenton's reagents. The present study deals with Fenton's degradation of a waste water containing Sulfinol-D. Batch experiments were carried out to determine the efficiency of treatment under a wide range of operating parameters. The parameters investigated are reagents concentrations (1 mol to 30 mol ratio) dosage, reaction time of Fenton treatment (30, 60, 120 min) and solid formation to monitor sedimentation percentage. From the previous study, it was observed pH 3 gave the best degradation efficiency. Additions of more Fe^{2+} salts reduce the degradation ability, whereas addition of more H_2O_2 increased the COD degradation slightly. It was also observed beyond a specific volume H_2O_2 the degradation ability was reduce. This was due to scavenging reaction. The results for these parameters are showed in form of COD degradation profile using Excel from spectrophotometer reading of the COD contains.

ACKNOWLEDGMENT

I would like to take this opportunity to acknowledge and thank everyone that has given me all the supports and guidance throughout the whole period of completing the final year project. Firstly, many thanks to the university and the Final Year Project coordinators that have coordinated and made the necessary arrangements, especially in terms of the logistics, for this study.

I must also acknowledge the endless help and support received from my supervisor and co-supervisor, Assoc. Prof. Ir. Abdul Aziz Omar and Mrs. Putri Nazatul Faizura bt Megat Khamaruddin throughout the whole period of completing the final year project. Their guidance and advices are very much appreciated.

I would also like to thank the lab technicians in UTP, for their endless support in terms of the preparation of logistics during the lab experiments for this study. Their continuous support and help throughout the whole period of experiments are very much appreciated.

Finally, many thanks to my fellow colleagues especially Nurul Ain binti Shurur and Ida Nurhidaya binti A.Aziz for the helps and ideas throughout the completion of this study. Thank you all.

TABLE OF CONTENTS

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 Background of Study

1.1.1 Amine Wastewater

Sour natural gas can contain undesirable compounds, including Hydrogen sulfide (H_2S), Carbonyl sulfide (COS), Carbon disulfide (CS_2) and mercaptans (Goar, 1971). As for that, amine is used in the treatment of sour natural gas and for this study, Sulfinol-D is the tertiary amine that been used in sweetening the gas. It is a highly water soluble compound that has been introduced into soils and ground waters at a number of sour gas processing plant sites.

The Sulfinol-D process uses a physical solvent, tetrahydrothiophene sulfone (sulfolane) and a chemical solvent, diisopropanolamine (DIPA) to remove H_2S, CO_2 and other contaminants from sour natural gas. This process is particularly effective at high H_2S concentrations (Goar, 1971), therefore is useful in liquefied natural gas (LNG) process , where process of the natural gas can contain up to 35% H_2S.

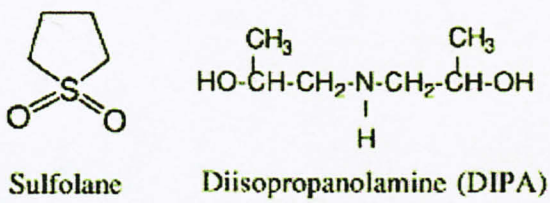


Figure 1.1: Structures of sulfolane and DIPA, which are the two major components used in the Sulfinol-D

Sulfolane and DIPA (Figure 1.1) are both highly water soluble compounds, and they have become ground water contaminants with the potential to migrate from the sour gas plant sites.

1.2 Problem Statement

1.2.1 Problem Identification

Advanced oxidation process is a good alternative to remove COD component in amine waste water from gas sweetening process of industry plant. The resulting amine waste water is to produce waste water of high chemical oxygen demand (COD) in the range 5000 to 25000 mg/L which highly affected the natural water stream of being discharge to the environment. Therefore, they must be effectively destroyed in industrial wastes before these are disposed off. There are stringent discharge limits for COD as per requirement from Department of Environment (DOE); from Parameter Limits of Effluent of Standard B, discharge of COD must not exceed 100 ppm. Consequently, reducing the concentration of COD is a necessary pretreatment prior to discharge to a biological waste treatment facility.

As for that, among Advanced Oxidation Processes (AOPs), Fenton's reagent has been efficiently used as a chemical process or wastewater treatment. Fenton's reagent is used to treat a variety of industrial wastes containing range of toxic organic compounds. Fenton system consists of ferrous salts combined with hydrogen peroxide under acidic condition. In varying the dose and optimum ratio of Fenton's Reagent, monitoring the efficiency of degradation of COD will be done in Sulfinol-D solution.

The economy of the process of oxidation with Fenton's reagent in relation to its treatment is extremely advantageous. No other version of the advanced oxidation is as competitive in this case. It has been recognize as a simple technology, low investment and operation costs (cheap reagents) offer an optimistic perspective for its industrial application. The only disadvantage is the formation of a deposit, which however can be greatly reduced. The hydrated deposits of ferric hydroxide $Fe(OH)_3$ form the reaction are the main problem in the industrial application of Fenton's process.

1.3 Objectives and Scope of Study

1.3.1 Objectives

The objectives of the research are:

1. To investigate the effect of Fenton's reagents dose on COD degradation efficiency.
2. To investigate the COD degradation efficiency using the optimum ratio of reagents for Sulfinol-D wastewater and correlate the formation of precipitation as the by-product from the treatment.
3. To investigate the effect of increasing the dosing of reagents time (either both or H_2O_2 only), hence increasing the reaction time and compared the percentage of COD removal with past research

1.3.2 Scope of Study

The study of the project will cover on the process of the Fenton's reagent that has been used to remove the COD in the waste water. The scope of the study is to evaluate the different hydrogen peroxide, H_2O_2 dosage (35.74, 44.67, 53.61& 62.54 ml), ferrous ion, FeSO4.7H20 dosage (2.03, 4.54, 6.08 & 8.11 g)), formation of solid and the reaction time of the treatment (30 min, 60 min, 120 min). The expected result of the experiment is the degradation of COD concentration. The graph of COD profile is being obtained from Excel-data to see the trends and effect of those parameters precisely. The result from this project will be compared with past research (different reaction time) to obtain expected result.

The research also will study the affect of formation of precipitation (solid formation) from amount of dosing reagents. This study is important to find the optimum environments discharges where the highest degradation of COD may occur with the less solid precipitated formation.

1.3.3 Flow of Study

Throughout this semester, the author needs to follow a certain flow as to execute her project as Figure 1.2 follow:

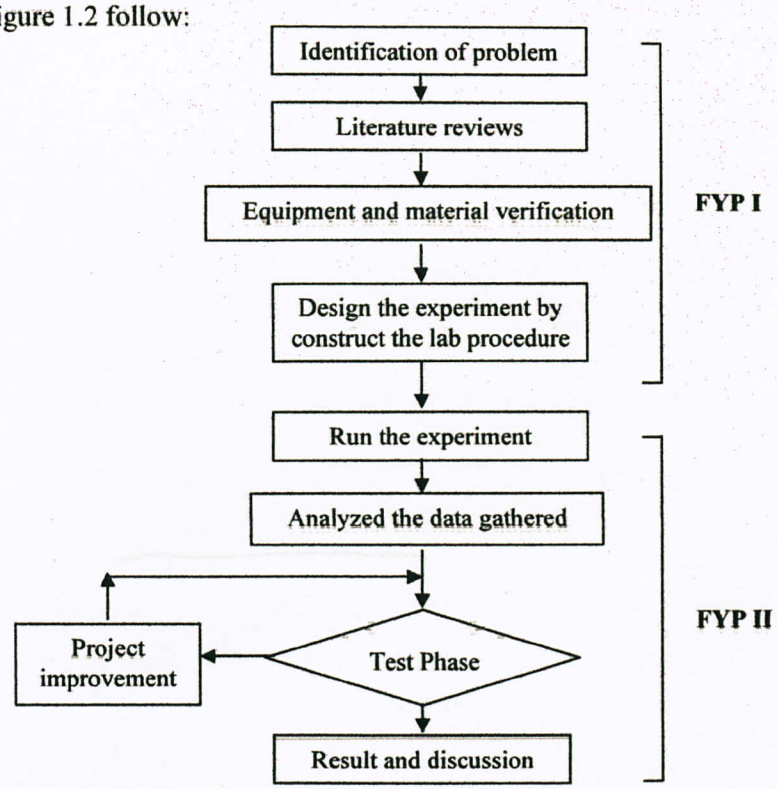


Figure 1.2 : Flow of Study for final year project (FYP) 1 and II

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 Fenton's Reagents

2.1.1 Conditions of Reaction

In this study, we explored the chemical oxidation of Sulfinol-D, selected as a model compound for aromatic amines, and the effect by hydroxyl radicals produced from Fenton's reagent. The reactivity of this system was first observed in 1894 by its inventor H.J.H. Fenton, but its utility was not recognized until the 1930's once the mechanisms were identified and proved to affect the being below:

- Organic pollutant destruction
- Toxicity reduction
- Biodegradability improvement
- BOD / COD removal
- Odor and color removal

This reagent is a mixture of hydrogen peroxide and ferrous iron that produces OH- radicals according to Walling (1975). Fenton's reaction (Fenton H. J.H, 1894) is one of the most effective methods of oxidation of organic pollutants that are oxidatively degraded by hydroxyl radicals generated from H_2O_2 in the presence of Fe^{2+} as a catalyst. When ferrous salts are used, the hydroxyl radical is produced immediately by the rapid reaction between ferrous ion and hydrogen peroxide (Equation 1). With ferric salts, the hydroxyl radical is produced in a two-stage process with the slow reaction between ferric ion and hydrogen peroxide (Equation 2) followed by the rapid reaction between the produced ferrous ion and additional hydrogen peroxide

$$H_2O_2 + Fe^{2+} \longrightarrow Fe^{3+} + OH^- + OH \ldots\ldots\ldots (1)$$

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + HO_2^- + H^+ \ldots\ldots\ldots (2)$$

Fenton's reagent possesses **three attractive features** for treating aromatic amines in wastes. **First**, the OH· radicals produced in equation (1) react with organic substances in a rapid manner with second-order rate constants in the range 107-101° $M^{-1}s^{-1}$. Such radicals have proved to effectively react with a variety of compounds such as alcohols, ethers, dyes, chlorinated phenols, pesticides, polycyclic aromatics, etc., in aqueous solutions and waste waters (Haag and Yao, 1992; Kuo, 1992; Pignatello, 1992). **Second**, the reagent components are easy to handle and environmentally friendly since the final decay products (water, oxygen and ferric hydroxide) introduce no further pollution. **Third**, hydrogen peroxide alone is currently used for industrial wastewater treatment to minimize the chemical oxygen demand and the additional cost of ferrous iron is quite low, so the treatment is quite economical. Moreover, ferrous iron can be regenerated electrolytically (Hsiao and Nobe, 1993; Tzedakis *et al.*, 1989).

For the Fenton reaction condition, the higher H_2O_2 concentration will influence the degree of organic mineralization. A study done by Matter et al. showed that the influence of higher concentration of Fe^{2+} increases the degree of decomposition of H_2O_2. From past research, the present of H^+ suggests that decomposition of H_2O_2 requires acidic environment for the production of desired ·OH radicals. As for that, the optimum pH is 3, and for pH adjustment, concentrated sulphuric acid, H_2SO_4 and 1 M sodium hydroxide, NaOH are needed to regulate the pH. Many report have been published on the use of Fenton's reagent to degrade pollutants such as MTBE (Methyl Tert Butyl Ether) (Neyens.J.B.A, 1998) aromatic amines (Arturo A.B and Dionysions, 2008), pharmaceutical waste (Casero, Silicia, Rubio and Dolores, 1997), petroleum refinery sour water (Tekin and Okan, 2006), phenol (Alessendra C., Antonio V.C and M'arcia) etc. All of these workers has successfully treated the waste water to a certain extend and were able to improved its biodegradability. It also noted that high volume of reagent will be used if complete mineralization of the wastewater is required.

2.1.2 Fe^{2+}/H_2O_2 Concentration Ratio - Solid Formation

The literature shows that apparently there is not an unique ratio between H_2O_2 and Fe^{2+} concentration that could be used to oxidize organic compounds. There is a degradation studies using 2-chlorophenol and ionic surfactants were reported employing $Fe^{2+}:H_2O_2$ molar ratio of 1:100 and 1:1, respectively (Huang et al., 1993; Kitis et al., 1999). As for $Fe^{2+}:H_2O_2$ molar ratio, some studies have mentioned that there is limit in this two portion of reaction which is in range of 1-30. This ratio need to be monitor as the increasing of Fe^{2+} dosage in the solution contribute to the formation of small quantities of sludge deposits after neutralization. The ferric hydroxide sludge, an additional product of Fenton's reaction, was formed in a low amount, up to 3-5% of total sludge volume after neutralization with CaO. Its stability and dewater ability were not determined. (K. Barbusiński, 2000)

Reaction rates with Fenton's Reagent are generally limited by the rate of. OH generation (i.e., concentration of iron catalyst) and less so by the specific wastewater being treated. Typical Fe: H_2O_2 ratios are 1:5-10 wt/wt, though iron levels < 25-50 mg/L can require excessive reaction times (10-24 hours). This is particularly true where the oxidation products (organic acids) sequester the iron and remove it from the catalytic cycle. Fenton's Reagent is most effective as a pretreatment tool, where COD's are > 500 mg/L. This is due to the loss in selectivity as pollutant levels decrease:

2.1.3 Fenton's Reagents procedure

The procedure requires:

- adjusting the wastewater to pH 3-5;
- adding the iron catalyst (as a solution of $FeSO_4$); and
- adding slowly the H_2O_2. If the pH is too high, the iron precipitates as $Fe(OH)_3$ and catalytically decomposes the H_2O_2 to oxygen -- potentially creating a hazardous situation.

2.2 Advanced Oxidation Process (AOPs)

Basically, oxidation process means converting to oxide which apply to metals, nonmetals, and organic matter. Oxygen is used as an oxidizer, because it is cheap and easily found which forms about 20% of air. Apparently, contaminants can be oxidized by four common reagents: ozone, hydrogen peroxide, oxygen and air. These procedures may also be combined with ultraviolet (UV) irradiation, ultrasonic vibrator and specific catalysts. A well known example of AOP is the use of Fenton's reagent. Advanced Oxidation Processes, refers to a set of chemical treatment procedures designed to remove organic and inorganic materials in waste water by oxidation. The contaminant materials can be converted into stable inorganic compounds such as water, carbon dioxide and salts.

AOPs, which involve the in situ generation of highly potent chemical oxidants such as hydroxyl radical (OH), have emerged as an important class of technologies for accelerating the oxidation and hence destruction of a wide range of organic contaminants in pollution solids, water and air. (Craig W.Jones, 1999). The hydroxyl radical is a powerful oxidant and a short lived, highly reactive, and non-selective reagent that is easy to produce. It has electrophonic properties and its reactions with appropriate sub-strate molecules are kinetically controlled usually very high second order rate constants, which are often close to the diffusion-controlled limit. (von Sonntag 1996). Kinetic reaction control refers to competing irreversible reactions in which the product composition is determined by the relative rates of product formation.

Several well-known approaches have been developed to generate hydroxyl radicals as shown in Table 2.1 ("Ultraviolet/chemical oxidation", 1996, page A-26).

Table 2.1: Oxidation Potential and Relative Potential of Common Oxidants

Oxidant	Reduction Half-Reaction	Potential E^o, V	Relative Potential, V[1]
Fluorine			
	$F_2 + 2H^+ + 2e^- \text{-----} > 2HF(aq)$	3.06	2.25
Ozone			
Acidic	$O_3 + 2H^+ + 2e^- \text{-----} > 2H_2O + O_2$	2.07	1.52
Basic	$O_3 + H_2O + 2e^- \text{-----} > O_2 + 2OH^-$	1.24	0.91
Hydrogen Peroxide			
Acidic	$H_2O_2 + 2H^+ + 2e^- \text{-----} > 2H_2O$	1.78	1.31
Basic	$HO_2^- + H_2O + 2e^- \text{-----} > 3HO^-$	0.85	0.62
Permangenate			
Acidic	$MnO_4^- + 4H^+ + 3e^- \text{-----} > MnO_2^- + 2H_2O$	1.67	1.23
Basic	$MnO_4^- + 2H_2O + 3e^- \text{-----} > MnO_2^- + 4OH^-$	0.59	0.43
Chlorine			
	$Cl_2 + 2e^- \text{------} > 2Cl^-$	1.36	1.00
Hypochlorite			
	$ClO^- + H_2O + 2e^- \text{-----} > Cl^- + 2OH^-$	0.90	0.66
Oxygen			
Acidic	$O_2 + 4H^+ + 4e^- \text{------} > 2H_2O$	1.23	0.90
Basic	$O_2 + 2H_2O + 4e^- \text{------} > 4HO^-$	0.40	0.29

AOP is used to decompose many hazardous compounds to requirement levels, without producing additional hazardous by-product or sludge. Advanced oxidation process refers to process in which oxidation of organic contaminants occurs primarily through reaction with hydroxyl radicals. This process has a rapid reaction rates and potential to reduce toxicity whilst possibly complete mineralization of organics treated. It does not concentrate waste for further treatment with methods such as membranes. Material that requires further treatment like spent carbon from activated carbon absorption is no longer been produce ("On-Site Flowback/Produced Water Treatment Alternatives", 2008, September 17)

AOP does not producing sludge and it is non selective pathway that allows multiple treatments organic at once. The contaminant materials can be converted into stable inorganic compounds such as water, carbon dioxide and salts. However, it still has disadvantages like the intensive capital; complex chemistry compound must tailor to

(O_3/UV), Hydrogen peroxide/ozone (H_2O_2/O_3) and Hydrogen peroxide/ozone/ultraviolet (H_2O_2/O_3/UV) processes can lead to different result as table 2.2 ("Advanced Oxidation Processes (AOP)" 2004) :

Table 2.2: Higher COD removal rates

Process	H_2O_2/O_3/Catalyst	O_3/UV/Catalysts	H_2O_2/O_3/UV/Catalyst
COD Removal	30%	49%	59%

Advanced oxidation process has a wide range of applications mainly for oxidation of refractory compounds, TOC & COD reduction in ("Advanced Oxidation Processes (AOP)" 2004):

1. Industrial (mainly gas) effluent treatment
2. Water recycling
3. Drinking water supplies
4. Industry of wastewater
5. Process water, ultra-pure water
6. Electronic & pharmaceutical industries
7. Medicinal baths, sanatoriums, hospitals
8. Cooling water systems
9. Fish hatcheries and farm

The oxidation of organics in the presence of ozone occurs via two pathways; one involving molecular ozone and the other involving the hydroxyl radical which is formed during the decomposition of oxygen. Oxidation via molecular oxygen is a highly selective, relatively slow, reaction. Oxidation via hydroxyl radical however is a very rapid and less selective process (Hoigne and Bader, 1983a and 1983b). The advanced oxidation processes promote the formation of hydroxyl radicals.

CHAPTER 3

METHODOLOGY

3.1 Literature Review

This is the steps to gain the information on the related theory involved for this project. Basically, the research is narrow down degradation of Sulfinol-D (COD degradation efficiency) and the Fenton's reagent for application in waste water treatment. A few series of work has been done to help the author execute her project which included:

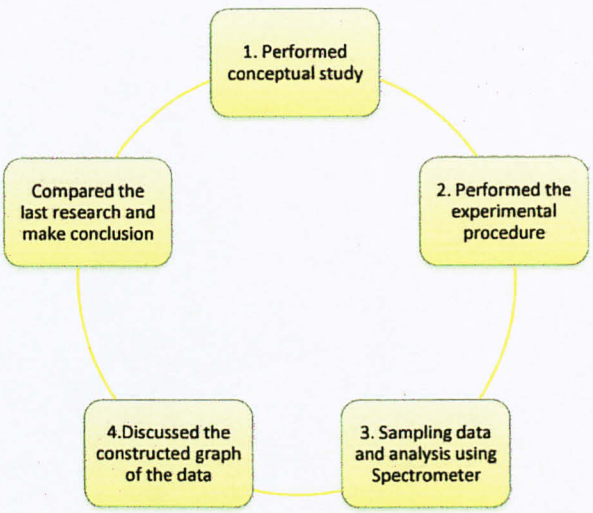


Figure 3.1: Scope of Work

Table 3.1: Gantt Chart

No	Task	No of Weeks													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Project Work Continue											Mid Term Break			
2	Submission of Progress Report 1														
3	Project Work Continue														
4	Submission of Progress Report 2														
5	Poster Exhibition														
6	Submission of Dissertation														
7	Oral Presentation														
8	Submission of Project Dissertation														

3.2 Experimental Study

Many factors affecting the COD degradation efficiency such as the effect of hydrogen peroxide, H_2O_2 dosage, ferrous ion, FeSO4.7H20 dosage, Sulfinol-D initial concentration and optimum pH. In this study, only dosages of the two reagents were monitored and correlated the dosage with the amount of solid formation. After got the optimum dosage of the reagents, another set experiment has been conducted to differentiate the effect of retention time of the reagents.

Hence, the experiment has been divided into three main parts. All parts of this experiment has been analyze from the records of a few set of data which are: COD concentration, sample pH and temperature reaction based on calculation molar ratio 1:30 (referred Appendix B). The categorized experiments are as follows

3.2.1 Categorized Experiment

i. Experiment 1

Manipulated variable: hydrogen peroxide, H_2O_2 dosage (35.74, 44.67, 53.61& 62.54 mL).

Constant variables: Ferrous ion dosage (4.054g), Sufinol-D concentration (0.5%), pH (3)

ii. Experiment 2

Manipulated variable: Ferrous ion, $FeSO_4.7H_20$ dosage (2.03, 4.54, 6.08 & 8.11 g)

Constant variables: hydrogen peroxide dosage (44.67 mL), Sulfinol-D concentration (0.5%), pH (3)

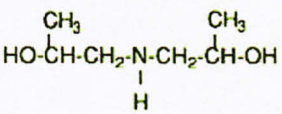
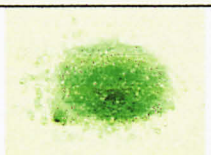
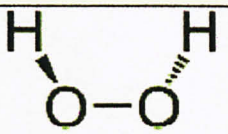
iii. Experiment 3

Manipulated variable: Reaction time (30 min, 60 min, 120 min)

Constant variables: Optimum dosage from previous experiment.

3.2.2 Chemical Substances Used

Table 3.2: Physical Properties of Chemical Substance Used

	Sulfolane	DIPA	Ferrous Iron(II)	hydrogen peroxide
Skeletal Formula/ 3D Model				
Molecular Formula	**$C_4H_6O_2S$**	**$C_6H_{15}O_2N$ @ $NH(CH_2CHOHCH_3)_2$**	**$FeSO_4.7H_20$**	**H_2O_2**
Molecular Weight, g/mol	**118.15**	**133.19**	**263.91**	**34.015**
Boiling point at 101.3 kPa, °C	**285**	**249**	**90**	**150.2**
Melting point at °C	**65-66**	**44.5**	**400 °C (decamp)**	**-20**
Solubility at 20°Cin Water, g/l	**Compatibility with water**	**Compatibility with water**	**25.6 g/100mL (anhydrous)**	**Miscible**
Usage for experimental study	Main solution in this project combining with DIPA to produce Sulfinol-D to have high COD concentration	Main solution in this project combining with sulfolane to produce Sulfinol-D to have high COD concentration	As catalyst in decomposition of hydrogen peroxide to form free radicals such as HO· (hydroxyl) and HOO·	As one of the Fenton's reagent. Hydrogen peroxide always decomposes (disproportionate) exothermically into water and oxygen gas spontaneously: $2\,H_2O_2 \rightarrow 2\,H_2O + O2$

3.1.3 Equipment Selection

1 Jacket glass reactor
2 Magnetic stirrer
3 DR5000 spectrophotometer
4 Thermometer
5 pH meter
6 Pump
7 Pipette
8 Beaker
9 COD TNTplus™ vials for the appropriate concentration range
10 Test Tube Rack
11 Rubber tubes

From the list of equipments above, the writer has done some research particularly on the main equipments such as UV visible spectrophotometer, pH probe and HACH 8000 COD vials for further familiarization and experimental setup.

a) DR5000 Spectrophotometer

This project has been using DR5000 spectrophotometer which involves the spectroscopy of photons in the UV-visible region. The spectrophotometer is a complex instrument used in measuring the absorbance of bio-molecules within the ultraviolet and visible light spectrum, similar to the one found in the laboratory. It is a conglomerate of light sources, wavelength selectors, optical systems, sample chambers, photo detectors, and meters functioning together to perform a specific task – to measure the COD contains of a sample. Procedure to checking the COD is in Appendix C

Figure 3.3: DR5000 spectrophotometer

b) pH Meter

pH meter is an electronic instrument used to measure the pH which means the level of acidity and alkalinity of a liquid. For this project, pH became one of the elements that need to be considered as the result. A typical pH meter consists of a

special measuring probe like a glass electrode that is connected to an electronic meter. The electronic meter will measure and display the pH reading for that solution. While taking the measurement, pH meter should be calibrated with buffered 7 and 10 before taking each of the reading since the glass electrode does not give a reproducible e.m.f. over longer periods of time.

Figure 3.4: pH Meter

c) HACH 8000 COD vials

The HACH 8000 COD vials are used as the medium to read COD contain in waste water sample. The mg/L COD results are defined as the mg of O_2 consumed per liter of sample under conditions of this procedure. In this procedure, the sample is heated for two hours with a strong oxidizing agent, potassium dichromate. Oxidizable organic compounds react, reducing the dichromate ion (Cr_2O_{72}–) to green chromic ion (Cr^{3+}). When the 3–150 mg/L colorimetric method is used, the amount of Cr6+ remaining is determined. When the 20–1500 mg/L colorimetric method is used, the amount of Cr^{3+} produced is determined. The COD reagent also contains silver and mercury ions. Silver is a catalyst, and mercury is used to complex chloride interferences. Test results for the 3 to 150 mg/L range are measured at 420 nm. Test results for the 20 to 1,500 mg/L COD range are measured at 620 nm.

Figure 3.5: COD sample in HACH 8000

3.3 Experimental Setup

3.3.1 Waste Preparation

Synthetic wastewater is prepared which is similar to commercial Sulfinol-D that was obtained from natural gas processing plant. The waste was been prepared prior all experiment as throughout the project, only 0.5% concentration just be to be used for each trial.

1. Mixed 500 mL of DIPA, 250 mL of Sulfolane and 250 mL of distilled water in 1 Liter volumetric flask.
2. Mark it as 100ppm standard solution

3.3.2 Develop standard curve for of COD concentration vs. % of Sulfinol-D

A standard curved for initial % of Sulfinol-D with concentration of 1-8% was performed for this project analysis. Below is the method to produce the calibration curve.

1. Prepared solutions from standard solution that have been prepared earlier with concentration of 1, 2, 3, 4, 5, 6, 7 and 8%
2. Solution from each concentration will be measured their COD analysis by HACH 8000 using DR5000 spectrophotometer
3. Results are in COD mg/L (ppm)
4. A graph of actual concentration versus measured concentration will be plotted

3.3.3 Experimental Setup for effect of parameters

After finish preparing the standard solutions, the test on the COD degradation were conducted as these procedures:

A. Fenton's reagent reaction

1. Experiment were conducted in the batch mode in a 1 L jacketed glass reactor with provisions for sampling, temperature and pH probes.
2. The reactor was placed on a magnetic stirrer
3. Water was passed through the jacket during the reaction in order to maintain the solution temperature at 30°C
4. The experiment were carried in manipulated reaction time. (30,60 and 120 minutes)
5. 500 ml of Sulfinol-D solution prepared to the required concentration and charged into the reactor
6. The pH solution was corrected before mixing in a weighted amount of $FeSO_4.7H_20$ crystals.
7. Then calculated amount of 30% H_2O_2 was added slowly in order to avoid excessive foaming
8. Sample were taken periodically throughout the experiment to determined COD. COD analysis were done using HACH 8000 using DR5000 spectrophotometer.

B. Sample analysis

1. Volume of sample taken for each sampling time was 2mL and this was mixed with 4mL of 1 M NaOH and necessary amount of distilled water was added for dilution purpose
2. The reason behind addition NaOH was to stop the reaction by removing excess H_2O_2 by increasing the pH of sample
3. The samples were heated up to 70°C to remove the remaining H_2O_2 for 20 minutes. This to ensure the H_2O_2 will not interfere with the COD value
4. The samples were also filtered using syringe filter to remove all precipitated iron

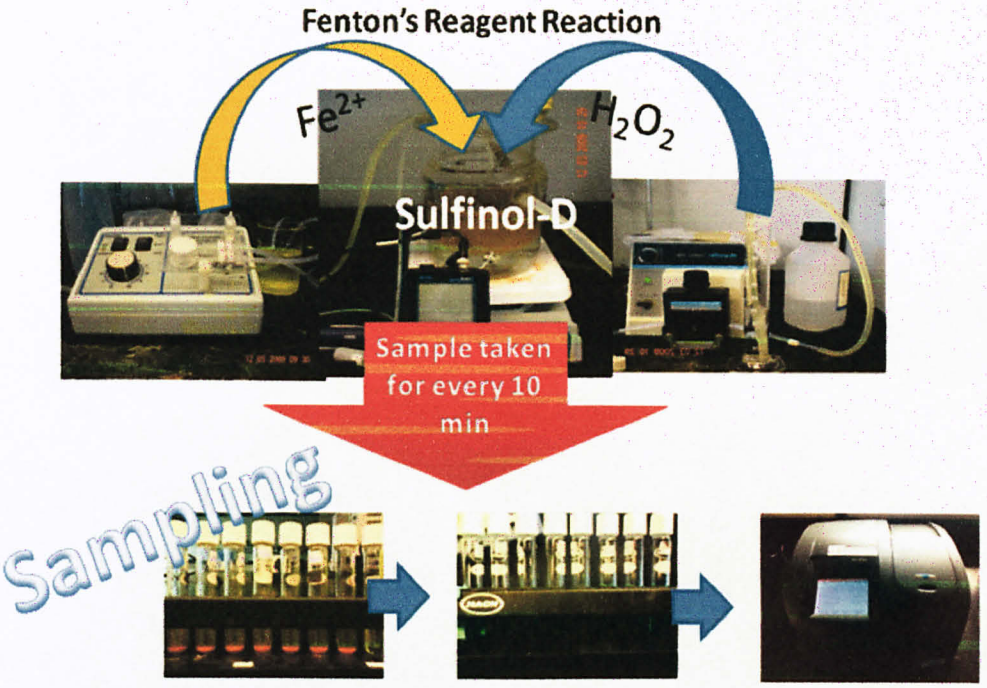


Figure 3.6: Illustrated figure for experimental setup

3.2.3 Experimental Setup for Total Suspended Solid.

The solid formations during the reaction of Fenton's reagent need to be identified as procedure below:

1. Obtain the tare weights of aluminum dishes each containing a glass fiber filter.
2. Assemble filtering apparatus, position the filter and begin suction. Wet filter with a small volume of distilled water to seat it.
3. Stir the reactor contents and then rapidly (so that it does not settle) measure 10mL for sample.

   [Hint: pour out small to avoid clogging when filter of well mixed sample and filter entire portion. Record the total volume filtered.]
4. Rinse the graduated cylinder with small amounts of distilled water and add to filter.
5. Carefully remove filter from filtration apparatus and transfer it back to the aluminum dish. Pinch sides of dish in a bit to protect the filter

from oven drafts. Place the aluminum dish into the 103°C oven to dry for at least one hour (leave drying overnight).

6. Transfer dish to desiccators, cool and weigh. Calculate the total suspended solids in terms of mg/L.

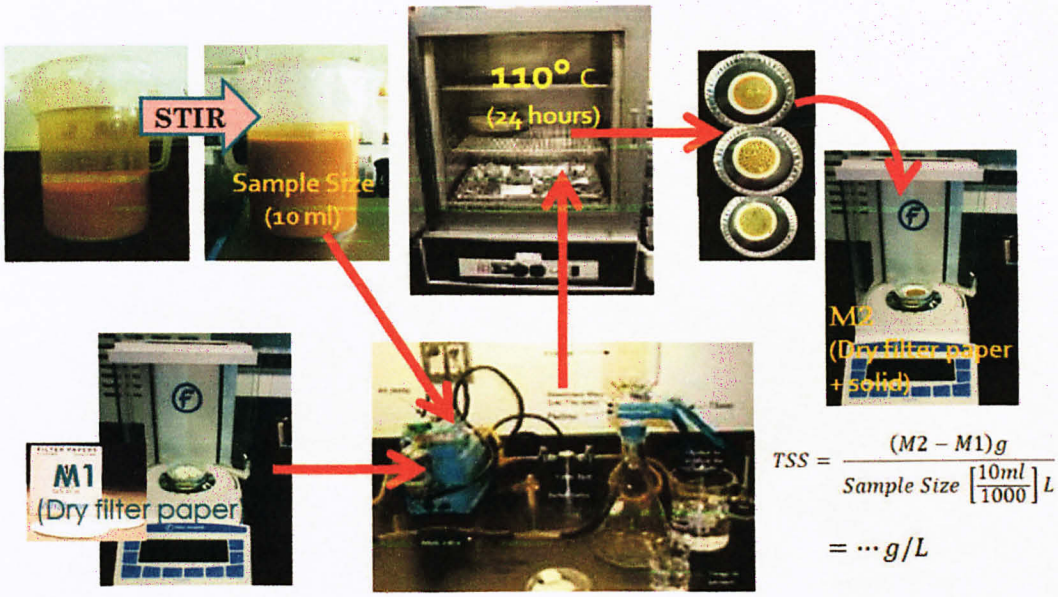


Figure 3.7: Illustrated figure for total suspended solid setup

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Results Analysis

After the experiments, all the results were tabulated as shown in shown in Appendix A. For the result analysis, the graph on degradation of Sulfinol-D by both reagents dosage can be obtained from the graph generated by Excel. Besides the results obtained, it could also be observed that there were traces of solid formation which is the formation of ferric hydroxide after the Fenton's reagents treatment. This observation is important to be noted as it may give an explanation of the future problems that must be cater due this treatment. This would be explained in greater detail in the later section.

In this section, the findings would be explained generally based on the trends that can be observed. The findings would be arranged according to the type of experiments done, i.e. the effect of dosage of H_2O_2, the effect of dosage of Fe^{2+}, formation of TSS and lastly time reaction of the treatment. After that, the result will be compared to past research as to investigate the molar ratio aspect. In the following section, these trends would be explained in greater details, offering the possible reasons and explanations to the trends observed.

4.1.1 Effect of Dosage of hydrogen peroxide, H_2O_2

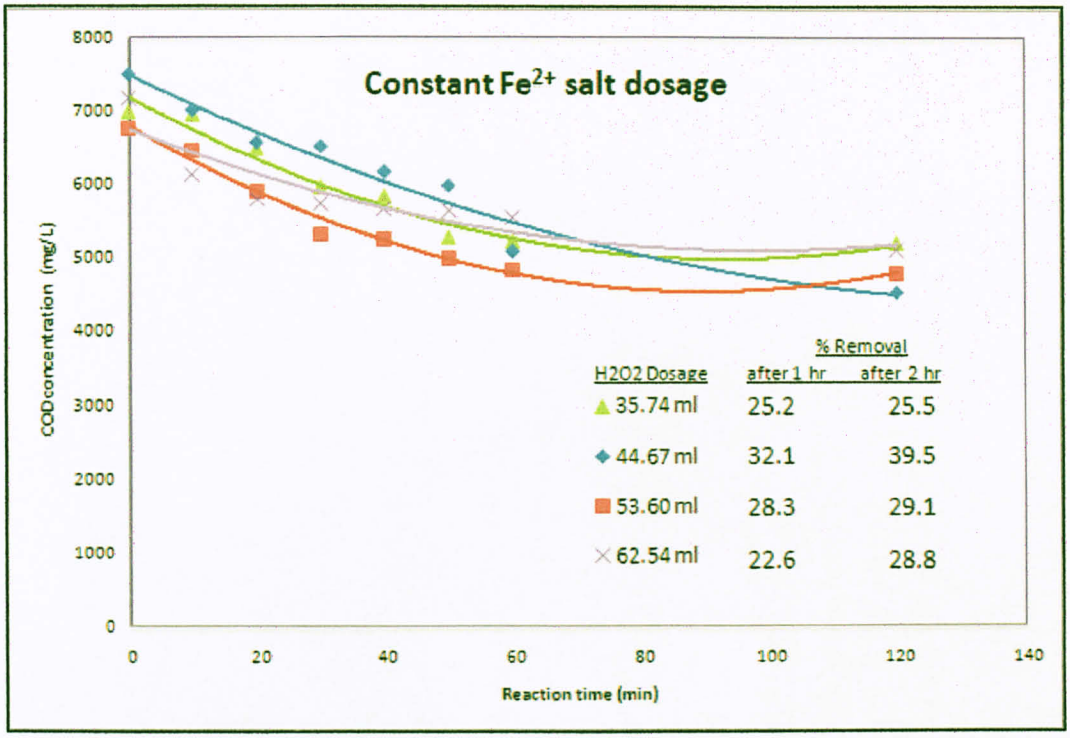


Figure 4.1: Graph of effect of the hydrogen peroxide, H_2O_2 dosage (COD degradation profile at 4.46 g $Fe2^+$, pH 3, T=30 °C)

From figure 4.1, it can be seen that the COD degradation profile when constant Fe^{2+} salt dosage were used with varying volume of H_2O_2 were dosage. The maximum degradation was at optimum dosage of 44.67 ml H_2O_2 where it gives 39.5 % of COD removal. At higher dosage there were no significant differences in COD degradation. Thus, it can be conclude that additional of more H_2O_2 would not be useful.

In Table 4.1 below indicates the TSS accumulate during four volume of H_2O_2 added. It can be conclude that the constant Fe^{2+} give no difference of solid formation during Fenton treatment. A possible reason for these observations will be discussed in the latter section.

Table 4.1: TSS formation of constant Fe^{2+} salt dosage.

Dosage	TSS (mg/L)
35.74 ml	3.06
44.67 ml	3.54
53.60 ml	2.85
62.54 ml	2.41

4.1.2 Effect of Dosage of Ferrous ion, $FeSO_4.7H_20$

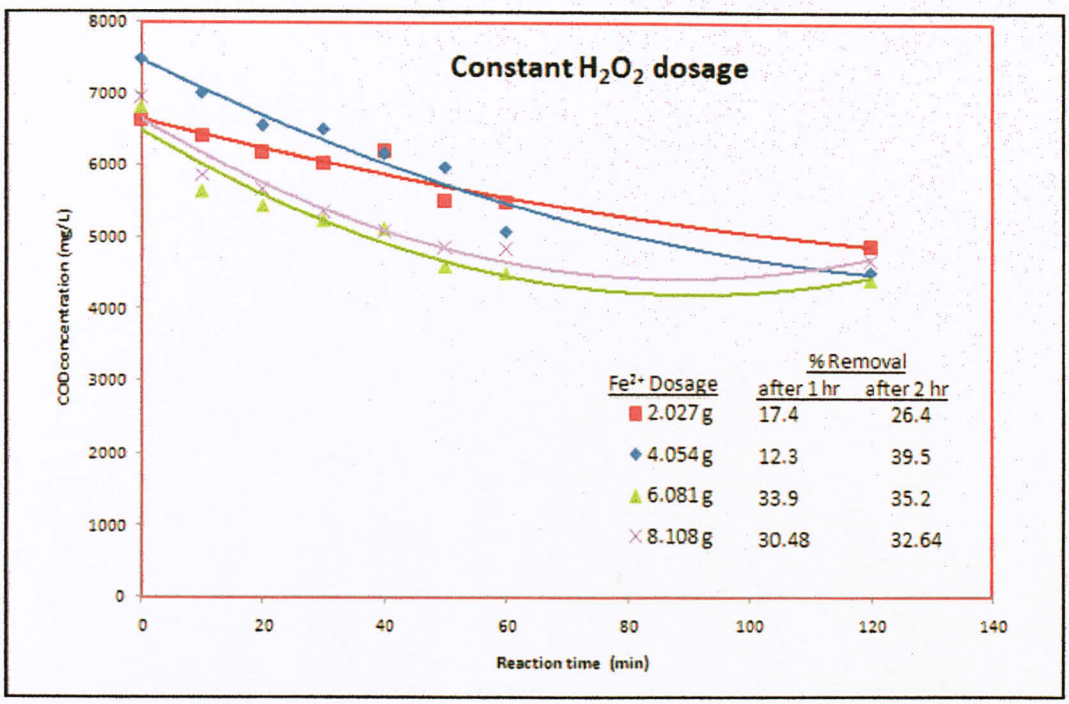


Figure 4.2: Graph of effect of the ferrous ion, $FeSO_4.7H_20$ dosage (COD degradation profile at 44.67 ml H_2O_2, pH 3, T=30 °C)

The weight of $FeSO_4.7H_20$ was varied for each run as shown in Figure 4.2. This set of experiment was carried out using constant dosage of H_2O_2 t of 44.67 ml which is from optimum dosage from previous set. The weigh of varied $FeSO_4.7H_20$ were calculated based on the Fe^{2+}:H_2O_2 molar ratio of 1:30. As can be seen from Figure 4.2 equimolar dosage (44.67 ml H_2O_2 and 4.054g of $FeSO_4.7H_20$) gave greatest COD degradation. It was observed that above the equimolar dosage, the COD degradation was lesser and it not give any degradation if more Fe^{2+} salt was added. This means excess amount of Fe^{2+} salt has been added which give scavenging reaction took place. A part from that, from Table 4.2 it showed that more amount of precipitate was collected from increasing the Fe^{2+} salt dosage.

Table 4.2: TSS formation of constant H_2O_2 dosage.

Dosage	TSS (mg/L)
2.027 g	2.76
4.054 g	3.53
6.081 g	7.93
8.108 g	13,03

4.1.3 Effect of Reaction Time of Fenton's Reagent Treatment

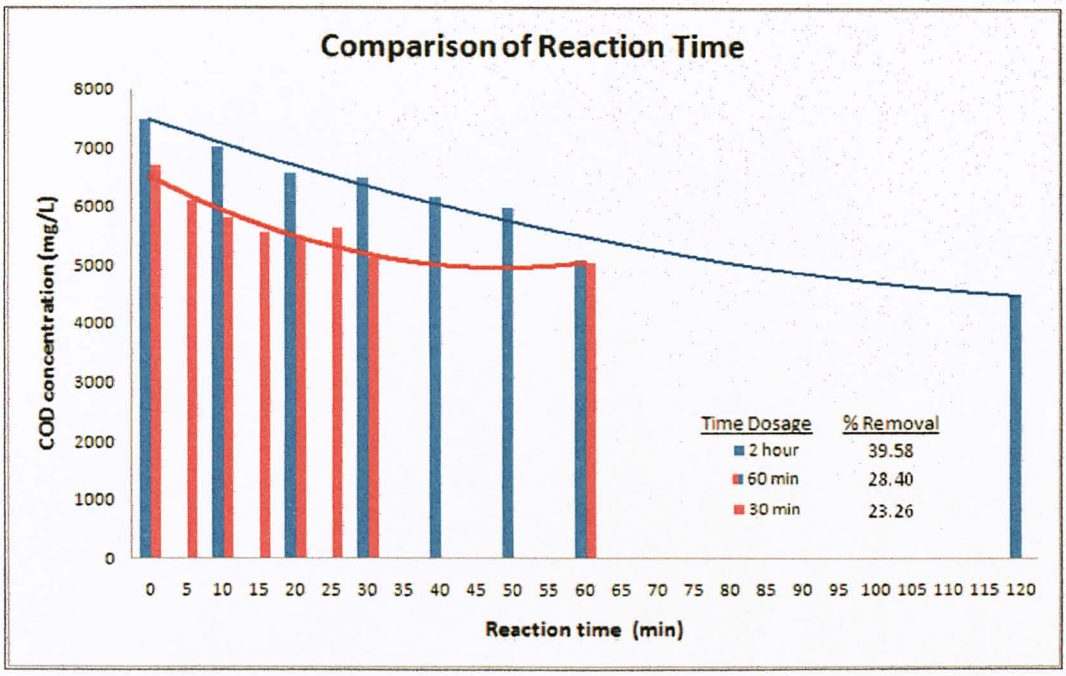


Figure 4.3: Graph of effect of the Reaction Time of Fenton's Reagent Treatment (COD degradation profile at 44.67 ml H_2O_2, 4.46 g $Fe2^+$, pH 3, T=30 °C)

Figure 4.3 showed the comparison of reaction time for optimum dosage of Fenton's Regent form previous set with addition of another 30 minutes experiment to compare between past researches. In this COD degradation profile, the percentages of COD removals are more when the both reagents have given more retention time. Thus, the reactions have more time to react with the waste where in two hour (120 minutes) reaction time give 39.6 % removal and in one hour (60 minutes) reaction time give 28.4 % removal compared to thirty minutes reaction time which gives only to 23.3 % of removal.

4.1.4 Effect of Molar Ratio of Fenton's Reagent Treatment

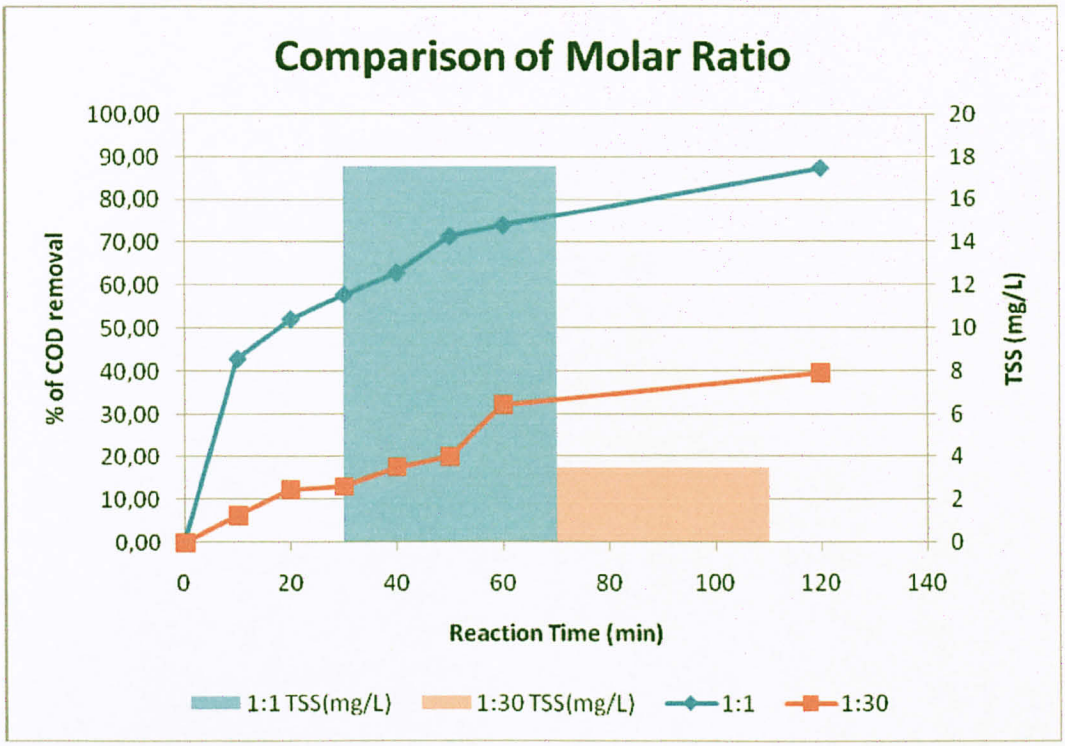


Figure 4.4: Graph of effect of the Molar Ratio of Fenton's Reagent Treatment

Figure 4.4 is showing the same trend in the percentage of COD removal by using Fenton's reagent treatment. The line graph showed the comparison between the current calculations of conducting during all run experiment which is 1:30 to the past research where it is 1:1. It can see that in current calculation, the result showed that the removal of COD is about half from the past research. But the column graph indicates that using the current calculation, the formation of TSS is reduced to five times from the past research.

4.2 Discussions

4.2.1 Effect of Dosage of hydrogen peroxide, H_2O_2 and Ferrous ion, $FeSO_4.7H_20$

From the COD degradation profile (figure 4.1 until 4.4), it can be seen that hydrogen peroxide and ferrous ion are the Fenton's Reagent to treated the waste of Sulfinol-D. It is being observed that when the waste was provided with more volume of H_2O_2 the COD degradation efficiency is increased. This observation is consistent with the observation from other studies and theories. As been reported, higher H_2O_2 concentration will influence the degree of organic mineralization, thus making it more crucial for effective treatment. Since, beyond an optimum amount of H_2O_2, the rate of total organic carbon removal will not be effective anymore. That is because there is limits to the amount of the reagents can be achieved maximum degradation, due to scavenging reactions take place when either one or both reagents are overdosed.

While for Ferrous ion, $FeSO_4.7H_20$ dosage increment also does increase the COD degradation. As reported in study done by Matter et. Al showed that influence of Fe^{2+} higher concentration of increases the degree of decomposition of H_2O_2. Throughout the reaction, Fe^{2+} acted as key for Fenton's oxidation as it is the limitation reactant. However, high concentration of Fe^{2+} seams to produce more solid formation. The formation of ferric hydroxide is one of the concerns in Fenton treatment as it can increase the operating cost and possibly necessitate an additional treatment to remove the excesses iron concentration in wastewater.

As a conclusion for these two parameters effect for this study is that the maximum degradation that can be achieve for this study at 0.5% Sulfinol-D is about 25-40%, even though more Fe^{2+} salt and H_2O_2 volume were added.

.

4.2.2 Effect of Reaction Time of Fenton's Reagent Treatment

Reaction time for Fenton's treatment is also crucial in evaluation its performance. That is because; although same amount of reagent dosage were used the effective of longer period is more significant. In the two hour of reaction give more percentage removal compared to one hour and thirty minutes treatment, because some H_2O_2 was not fully reacted with the waste. This retention time aspect is important in designing this waste treatment plant.

4.2.3 Effect of Molar of Fenton's Reagent Treatment

From the graph obtained in Figure 4.4, it shows as time goes by, the percentage COD removal is increased even though the percentage of past study is highly effective compared to current calculation which only reduce COD up to 39.5 %. These projects implement such value of ratio because this study is a sequel project of Wastewater Treatment Plant for Malaysia Liquid Natural Gas (MLNG)'s absorber. Due to that, previous researches have done calculation from 1: 1 mol ratio to 1:20 mol ratio. As for the author, she need to continue the work in varying the molar ratio up to 30 as being stated in literature review that limit range for Fenton's Reagents is between 1-30.

4.2.4 Procedure and Measurement during Experiment

The data obtained throughout the research shows slightly inconsistency when some of the sample reading may differ from original trends. In this situation, the main concern is due to the operational error while doing the experiment. The other parameters such as pH, initial Sulfinol-D concentration and temperature does effect the degradation of COD. To further identify those effects, the author has found some journal that theoretically doing the same concept which is to see the trends of degradation of COD while varying some parameters such as initial concentration and pH. The result can be additional reference and predicted result for her final year project (FYP). From journal and past research, COD profiles have been obtained from the same method in this project in 30 minutes reaction time. Fenton's oxidation

process was found to be able to degrade the COD of a Sulfinol-D solution to more than 50% at equimolar dosage for all parameters.

1) Constant Fe^{2+} salt dosage:

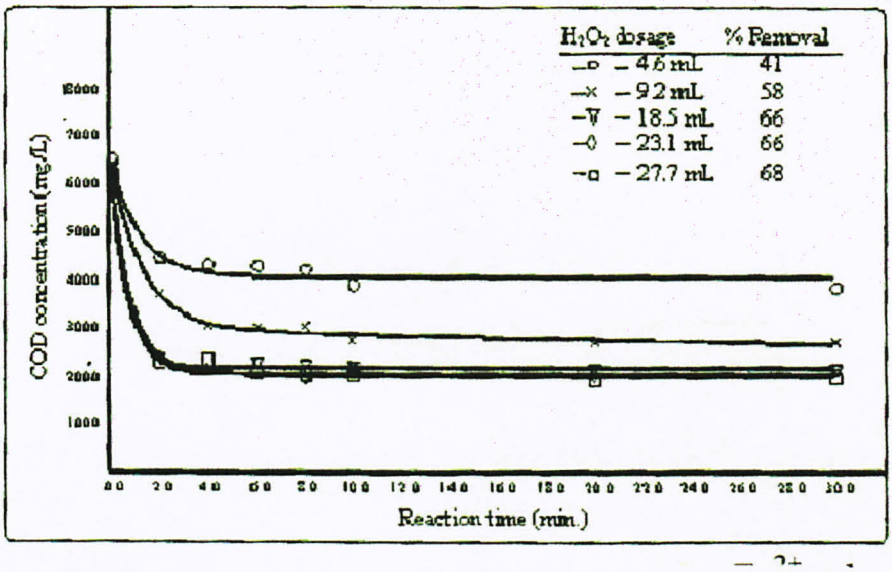


Figure 4.5: COD degradation profiles at 45g Fe^{2+} salt dosage, pH = 3, T= 30C, different H_2O_2 dosage

2) Constant H_2O_2 dosage:

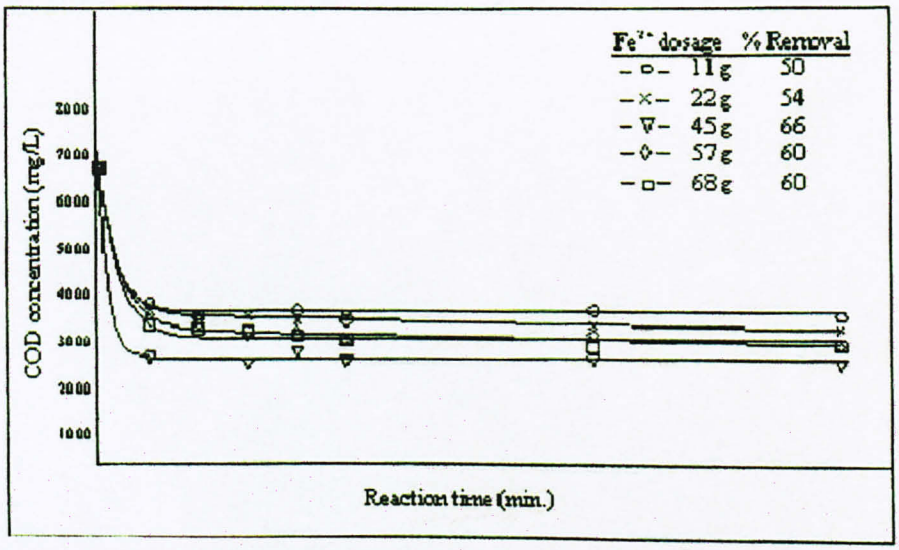


Figure 4.6: COD degradation profiles at 18.5 mL H_2O_2 dosage, pH = 3, T= 30C, different Fe^{2+} dosage

3) Optimum pH :

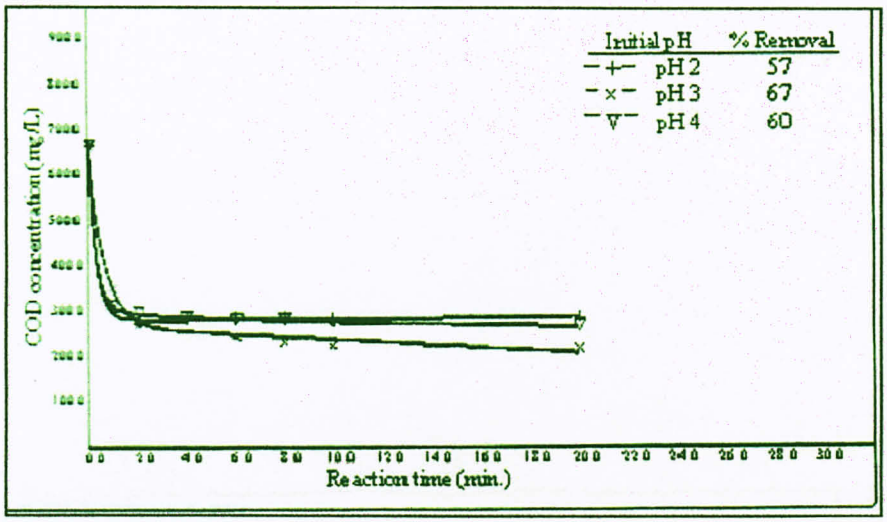


Figure 4.7 : COD degradation of 0.5 % Sulfinol-D at various initial pH

4) Constant Fenton's reagents ratio dosage :

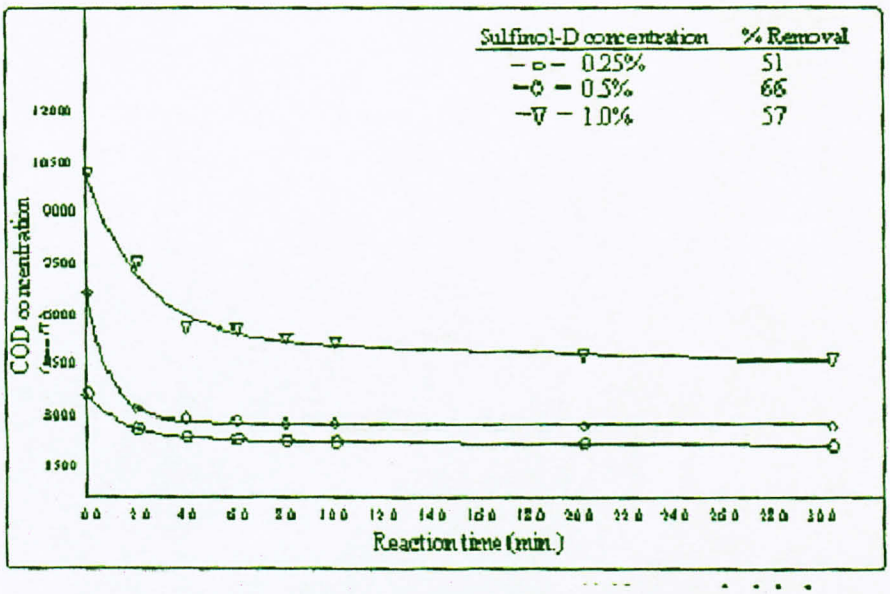


Figure 4.8 : COD degradation of 0.5 % Sulfinol-D at various initial concentration

From COD degradation profile of Figure 4.5-4.8, though the experiment is in 30 minutes, the trend of data is expected to be same. COD profile gain from the same procedure where the COD concentrations were analyzed in the spectrophotometer. From the graph, the optimum pH was found to be at 3. Another observation is the dependence of degradation ability to Fenton's reagents. Greater volume of H_2O_2 played a greater role in achieving better degradation compared to higher Fe^{2+} amount

However, the amount added needs careful consideration as excessive amount can lead to scavenging reaction which will not bring any benefits towards treatment of waste water.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

Many of the current development and investigations on the utilization of Advance Oxidation Process (AOPs) in treating waste water. From all AOP treatment, Fenton's Reagent reaction can be considered as one of agent to oxides the waste contains in waste water stream. As for that, studies done on parameter in enhancing this treatment will prove to be a key area of scientific application in the future decades.

From the studies done, conclusion that can be drawn out from this project paper is **first,** Fenton's reagents are a good treatment to remove the COD concentration from amine waste water and other industrial effluent. With the presence of hydrogen peroxide, it tends to remove more COD. That is why hydrogen peroxide alone is currently used for industrial wastewater treatment to minimize the chemical oxygen demand and the additional cost of ferrous iron is quite low, so the treatment is quite economical. Moreover, ferrous iron can be regenerated electrolytically.

Second, the increasing the time reaction for the Fenton treatment takes place gives more percentage of removal of COD. Allowing more retention time for the reagent to have complete reaction to react with the waste, will reduce COD concentration significantly till it can reach to biological treatment influent condition.

As for the optimum data from this study with calculation of 1:30 molar ratio give the both Fenton's Reagent dosage are 44.67 ml for H_2O_2 and 4.54 g for $FeSO_4.7H_20$ which react in two hour of reaction to reach 39.5% of COD removal.

REFERENCES

1. E.Anne Greene, Lisa M.Gieg, Debora L.Coy and Philip M. Fedorak, Sulfolane biodegradation potential in aquifer sediments at sour natural gas plant sites, *Water Research,* 32(12), 1998, pp 3680-3688
2. E. Neyens. J. Baeyens, A review of classic Fenton's per oxidation as an advanced oxidation technique. *Journal of' Hazardous Materials,* B98. 2003.
3. Arturo A. Burbano, Dionysios D Dionysiou, Mkaram T. Suidan, Effect of oxidant-to-substrate ratios of the degradation of MTBE with Fenton reagent, *Water Research*, 42,2008, pp.3225-3239
4. [4]Imaculada Casero, Dolores Silicia, Soledad Rubio, Dolores Perez-Bendito, Chemical degradation of aromatic amines by Fenton's reagent, *Water Research*, 31(8),1997, pp.1985-1995
5. Huseyin Tekin, Okan Bilkay, Selale S. Ataberk, Tolga H. Balta, I. Haluk Ceribasi, F. Dilek Sanin, Filiz B. Dilek, Ulku Yetis, Use of Fenton oxidation to improve biodegradability of a pharmaceutical waste water, *Journal of Hazardous Materials*, 136(2), 2006, pp. 258-265
6. Alessandra Coelho, Antonio V. Castro, M´arcia Dezotti, G.L. Sant'Anna Jr., Treatment of petroleum refinery sour water by advanced oxidation processes, *Journal of Hazardous Materials*, 137, 2006. Pp 178-184
7. [7]V. Kavitha, K. Palanivelu, The role of ferrous ion in Fenton and photo-Fenton processes for the degradation of phenol, *Chemosphere,* 55, 2004, p.p 1235-1243.
8. L Matter, E V C Rosa, J Berto, A X R Correa, P R Schwingel, C Cm Redetski, A simple methodology to evaluate influence of H2O2 and Fe2+ concentration on the mineralization and biodegradability of organic compounds in water and soil contaminated with crude petroleum, *Journal of Hazardous Materials*, 149, 2007, pp. 379-386

9. Putri Nazatul Faizura bt Megat Khamaruddin, *Development of a Hybrid Technology Combining Advanced Oxidation and Biological Processes for Degradation of Spent Absorbent.* University Technology Petronas.
10. Thomas Oppenlander, *Photochemical Purification of Water and Air,2003*
11. Robert W. Peters and Jan Mohammad (2004): *Comparison of Integrated AOP System for BTEX Removal from Solution:* Department of Civil and Environmental Engineering, University of Alabama at Birmingham,
12. Sven Erik Jørgensen (1934). *Industrial Waste Water Management (science 5)*. Netherland: Elsevier Scientific Publishing Company
13. (DEPARTMENT OF THE ARMY U.S. Army Corps of Engineers CEMP-RT Washington, Ultraviolet/Chemical Oxidation, DC 20314-1000, 1996)
14. Bruce T. Ketrick. (2004, February 1). *Safer products, environment with wastewater treatments.* Retrieved from http://www.isa.org/Template.cfm?Section=Communities&template=/TaggedPage/DetailDisplay.cfm&ContentID=33759
15. Spartan Environment Technologies. (2004). *Advanced Oxidation Processes (AOP).* Retrieved from
    a. http://www.spartanwatertreatment.com/about-spartan.html
    b. http://www.spartanwatertreatment.com/advanced-oxidation-processes.html
16. Wikipedia, the free encyclopedia. (2009, September 21).
    a. http://en.wikipedia.org/wiki/Sulfolene
    b. http://en.wikipedia.org/wiki/hydrogen_peroxide
    c. http://en.wikipedia.org/wiki/iron_II_sulfide
17. http://www.sciencedirect.com/
18. http://www.wikipedia.com
19. http://en.wikipedia.org/wiki/Electromagnetic_spectrum
20. http://www.google.com/patents
21. http://www.chemyq.com/En/xz/xz1/2804oluqo.htm

APPENDICES

Appendix A: Experimental Data and Tabulated Calculation Results

Table A.1: Recorded results for effect of Dosage of hydrogen peroxide, H_2O_2

35.74 ml			
min	COD	COD x DF	% removal
0	1394	6970	0
10	1386	6930	0,57
20	1294	6470	7,17
30	1191	5955	14,56
40	1165	5825	16,43
50	1054	5270	24,39
60	1043	5215	25,18
120	1039	5195	25,47
44.67 ml			
min	COD	COD x DF	% removal
0	1498	7490	0
10	1402	7010	6,408545
20	1313	6565	12,3498
30	1302	6510	13,08411
40	1234	6170	17,6235
50	1196	5980	20,16021
60	1017	5085	32,10948
120	905	4525	39,58611

53.60 ml			
min	COD	COD x DF	% removal
0	1349	6745	0
10	1288	6440	4,521868
20	1180	5900	12,5278
30	1063	5315	21,20089
40	1050	5250	22,16457
50	1000	5000	25,87102
60	968	4840	28,24314
120	957	4785	29,05856
62.54 ml			
min	COD	COD x DF	% removal
0	1433	7165	0
10	1226	6130	14,45
20	1157	5785	19,26
30	1145	5725	20,10
40	1132	5660	21,00
50	1128	5640	21,28
60	1109	5545	22,61
120	1020	5100	28,82

Table A.2: Recorded results for effect of Dosage of Ferrous ion, $FeSO_4.7H_20$

2.027 g			
min	COD	COD x DF	% removal
0	1329	6645	0
10	1283	6415	7,76
20	1238	6190	11,00
30	1207	6035	13,23
40	1244	6220	10,57
50	1103	5515	20,70
60	1098	5490	21,06
120	978	4890	29,69
4.054 g			
min	COD	COD x DF	% removal
0	1498	7490	0
10	1302	6510	4,62
20	1234	6170	9,60
30	1196	5980	12,38
40	1017	5085	25,49
50	1313	4378	27,71
60	1102	4483	29,88
120	905	4525	33,70

6.081 g			
min	COD	COD x DF	% removal
0	1365	6825	0
10	1129	5645	17,29
20	1089	5445	20,22
30	1049	5245	23,15
40	1026	5130	24,84
50	921	4605	32,53
60	901	4505	33,99
120	884	4420	35,24
8.108 g			
min	COD	COD x DF	% removal
0	1391	6955	0
10	1173	5865	15,67
20	1133	5665	18,55
30	1070	5350	23,08
40	1017	5085	26,89
50	975	4875	29,91
60	967	4835	30,48
120	937	4685	32,64

Table A.3: Recorded results for of the Reaction Time of Fenton's Reagent Treatment

30 min			
min	COD	COD x DF	% removal
0	1337	6685	0,00
5	1220	6100	8,75
10	1161	5805	13,16
15	1111	5555	16,90
20	1096	5480	18,03
25	1125	5625	15,86
30	1026	5130	23,26

2 hour			
min	COD	COD x DF	% removal
0	1498	7490	0,00
10	1402	7010	6,41
20	1313	6565	12,35
30	1302	6510	13,08
40	1234	6170	17,62
50	1196	5980	20,16
60	1017	5085	32,11
120	905	4525	39,59

Table A.4: Recorded results for effect Molar Ratio of Fenton's Reagent Treatment

Time (min)	Molar Ratio			
	1:1		1:30	
	COD	% removal	COD	% removal
0	6415,5	0,00	7490	0,00
10	3955,2	42,77	7010	6,41
20	4215,0	52,02	6565	12,35
30	3869,6	57,71	6510	13,08
40	2922,4	62,85	6170	17,62
50	2203,2	71,40	5980	20,16
60	2026,2	73,86	5085	32,11
120	704,0	87,19	4525	39,59
TSS(mg/L)	17,56		3,53	

Appendix B: Calculation Results of 1:30 Molar Ratio

Hydrogen peroxide

Sulfinol-D COD ≈ 7000 mg/L

H_2O_2 → [O] ½ atom of O= oxidation of half of oxygen atom

MW of H_2O_2 = 34 g/mol

MW of O = 8 g/mol

Density of H_2O_2 = 1.11 g/ml

Mole H_2O_2= $\frac{7000mg/L}{8g/mol} = 0.875$ mole

Mass H_2O_2=0.875 mole x 34 g/mole = 29.75 g H_2O_2 of 100%

For 30% H_2O_2, mass = $29.75\ g \times \frac{100}{30} = 99.17\ g$

Volume of 30 % H_2O_2 = $99.17\ g \times \frac{1\ ml}{1.11g} = 89.34\ ml$

For initial molar ratio of 1:30

Amount of Fe^{2+}

MW of Fe^{2+} = 55 g/mole

MW of $FeSO_4$ = 278 g/mole

Initial molar ratio H_2O_2 /Fe^{2+} = 30

mole Fe^{2+} = 0.875/ 30 = 0.0292 mole

Mass Fe^{2+} = 0.0292 mole x 55 g/mole = 1.604 g Fe^{2+}

Mass of $FeSO_4.7H_2O$ = $1.604\ g\ Fe^{2+} \times \frac{278\frac{g}{mole}FeSO4}{55\frac{g}{mole}Fe}$ = 8.108 g FeSO4

Molar ratio = 30

Mole H_2O_2= 0.875 mole

Mole Fe = 0.029 mole

Mass Fe = 1.641 g

Mass FeSO4 = 8.108 g

1st Trial

FeSO4 = 8.108 g, H_2O_2= 89.34 ml @ pH 3 @ 2 hr << for 1 litter of waste

for 500 ml of waste = FeSO4 = 4.045 g, H_2O_2= 44.67 ml @ pH 3 @ 2 hr (120 min)

Appendix C: Procedure to Checking the COD Using HACH 8000

Oxygen Demand, Chemical

★Method 8000

TNTplus™

Reactor Digestion Method[1]

LR (TNT821, 3–150 COD);
HR (TNT822, 20–1500mg/L COD)

Scope and Application: For water, wastewater; digestion is required;
3–150 mg/L and 20– 1500 mg/L COD ranges are USEPA approved for wastewater analyses[2]

[1] Jirka, A.M.; Carter, M.J., *Analytical Chemistry*, 1975, 47(8), 1397
[2] *Federal Register*, April 21, 1980, 45(78), 26811-26812

Test Preparation

Before starting the test:

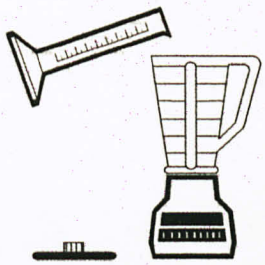
Please read *Safety Advice* and *Expiration Date* on package.
Some of the chemicals and apparatus used in this procedure may be hazardous to the health and safety of the user if inappropriately handled or accidentally misused. Please read all warnings and associated MSDS sheets.
To run the optional blank for a set of samples, see Blanks for Colorimetric Determination on page 3.
Spilled reagent will affect test accuracy and is hazardous to skin and other materials. Be prepared to wash spills with running water
Wear appropriate eye protection and clothing for adequate user protection. If contact occurs, flush the affected area with running water. Review and follow instructions carefully.
Store unused (light-sensitive) vials in closed box.

Collect the following items:	**Quantity**
Blender	1
DRB200 Reactor with 13-mm wells (use adapters with 16-mm holes)	1
COD TNTplus™ vials for the appropriate concentration range	varies
Pipettor for 2.0 mL Sample	1
Pipettor Tip	1
Test Tube Rack	2

Note: *Reorder information for consumables and replacement items is on page 5.*

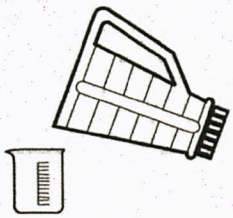
1. Turn on the DRB200 Reactor. Preheat to 150 °C.

Note: *For DRB 200 Reactors with 16-mm wells, insert a16-mm to 13-mm adapter sleeve into each well* ***before*** *turning on the reactor.*



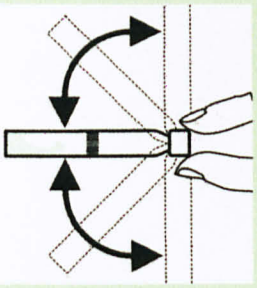
2. Homogenize 100 mL of sample for 30 seconds in a blender. For samples containing large amounts of solids, increase the homogenization time.

If the sample does not contain suspended solids, omit steps 1 and 3.



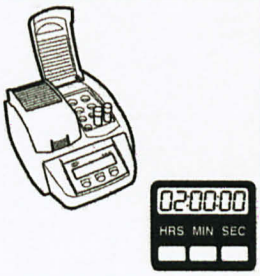
3. To help assure that a representative portion of sample is analyzed, pour the homogenized sample into a 250-mL beaker and gently stir with a magnetic stir plate.

4. Carefully pipet 2.0 mL of sample into the vial. Cap and clean the outside of the vial.



5. Hold the vials by the cap over a sink. Invert gently several times to mix. The sample vials will become very hot during mixing.

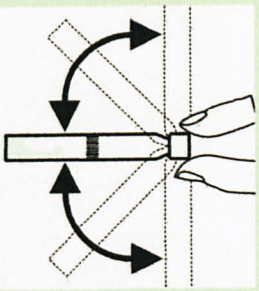
Place the vials in the preheated DRB200 Reactor. Close the protective lid



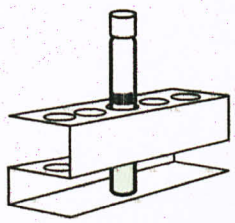
6. Heat the vials for two hours.

7. Turn the reactor off.

Wait about 20 minutes for the vials to cool to 120 °C or less.



8. Invert the vial several times while still hot.



9. Place the vial into a rack to cool to room temperature.

10. Thoroughly clean the outside of the vial.

11. Insert the vial into the cell holder. Close the lid.

The instrument automatically reads the barcode, then selects and performs the correct test.

Results are in mg/L COD.

Blanks for Colorimetric Determination

A reagent blank can be measured, and the value subtracted from the results of each test performed using the same reagent lot number. The blank may be used repeatedly for measurements using the same lot of vials. Store it in the dark, and monitor decomposition by measuring its concentration periodically.

To subtract the value of the blank from a series of measurements, measure the blank per step 11. Press **OPTIONS>MORE>REAGENT BLANK**. Select **ON**.The measured value of the blank should be displayed in the highlighted box. Press **OK** to accept this value. The reagent blank value will now be subtracted from all results until the function is turned off, or a different method is selected. Alternately, the blank can be recorded and entered at any later time by pressing the highlighted box and using the keypad to enter the value.

Interferences

Chloride is the primary interference when determining COD concentration. Each COD vial contains mercuric sulfate that will eliminate chloride interference up to 2000 mg/L Cl^-.

Sampling and Storage

Collect samples in glass bottles. Use plastic bottles only if they are known to be free of organic contamination. Test biologically active samples as soon as possible. Homogenize samples containing solids to assure representative samples. Samples treated with sulfuric acid* to a pH of less than 2 (about 2 mL per liter) and refrigerated at 4 °C can be stored up to 28 days. Correct results for volume additions.

* See Optional Reagents and Apparatus on page 5.

Accuracy Check

Standard Solution Method

1. Check the accuracy of the 3 to 150 mg/L range with a 100 mg/L standard. Prepare by dissolving 85 mg of dried (120 °C, overnight) potassium acid phthalate (KHP) in 1 liter of deionized water. Use 2 mL as the sample volume. The result should be 100 mg/L COD. Or dilute 10 mL of 1000-mg/L COD Standard Solution to 100 mL to produce a 100-mg/L standard.

2. Check the accuracy of the 20 to 1,500 mg/L range by using either a 300 mg/L or 1000 mg/L COD Standard Solution. Use 2 mL of one of these solutions as the sample volume; the expected result will be 300 or 1000 mg/L COD respectively. Or, prepare a 500 mg/L standard by dissolving 425 mg of dried (120 °C, overnight) KHP. Dilute to 1 liter with deionized water.

Method Performance

Precision
Standard: 75 mg/L COD (Low Range), 750 mg/L COD (High Range)

Program	Range (mg/L)	95% Confidence Limits of Distribution
TNT821	3–150	72–78 mg/L COD
TNT822	20–1500	736–764 mg/L COD

Sensitivity

Program	Portion of Curve	ΔAbs	ΔConcentration
TNT821	Entire range	0.010	3.8 mg/L COD
TNT822	Entire range	0.010	26.8 mg/L COD

Summary of Method

The mg/L COD results are defined as the mg of O_2 consumed per liter of sample under conditions of this procedure. In this procedure, the sample is heated for two hours with a strong oxidizing agent, potassium dichromate. Oxidizable organic compounds react, reducing the dichromate ion ($Cr_2O_7^{2-}$) to green chromic ion (Cr^{3+}). When the 3–150 mg/L colorimetric method is used, the amount of Cr^{6+} remaining is determined. When the 20–1500 mg/L colorimetric method is used, the amount of Cr^{3+} produced is determined. The COD reagent also contains silver and mercury ions. Silver is a catalyst, and mercury is used to complex chloride interferences. Test results for the 3 to 150 mg/L range are measured at 420 nm. Test results for the 20 to 1,500 mg/L COD range are measured at 620 nm.

Consumables and Replacement Items

Required Reagents

Description	Quantity/Test	Unit	Cat. No.
Select the appropriate TNTplus™ COD Digestion Reagent Vial:			
Low Range, 3 to 150 mg/L COD	1–2 vials	25/pkg	TNT821
High Range, 20 to 1500 mg/L COD	1–2 vials	25/pkg	TNT822

Required Apparatus

Description	Quantity/Test	Unit	Cat. No.
DRB200 Reactor, 115 V, 15 x 13 mm (1 block)	1	each	LTV082.53.21001
Pipet, variable volume, 1–5 mL	1	each	27951-00
Pipet Tips, for 27951-00 pipet	1	100/pkg	27952-00
Test Tube Rack, 13-mm	1–2	each	24979-00

Recommended Standards

Description	Unit	Cat. No.
COD Standard Solution, 300-mg/L	200 mL	12186-29
COD Standard Solution, 1000-mg/L	200 mL	22539-29
Potassium Acid Phthalate, ACS	500 g	315-34
Oxygen Demand Standard (BOD, COD, TOC), 10-mL ampules	16/pkg	28335-10
Wastewater Influent Standard, for mixed parameters (NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC)	500 mL	28331-49
Wastewater Effluent Standard, for mixed parameters (NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC)	500 mL	28332-49

Optional Reagents and Apparatus

Description	Unit	Cat. No.
Beaker, 250 mL	each	500-46H
Blender, 2-speed, 120 VAC	each	26161-00
Blender, 2-speed, 240 VAC	each	26161-02
DRB200 Reactor, 115 V, 15 x 13 mm (2 blocks)	each	LTV082.52.23001
Stir Plate, magnetic	each	28812-00
Stir Bar, octagonal	each	20953-52
Sulfuric Acid, ACS	500 mL	979-49
TNTplus™ Reactor adapter sleeves, 16-mm to 13-mm diameter	5/pkg	28958-05

FOR TECHNICAL ASSISTANCE, PRICE INFORMATION AND ORDERING:
In the U.S.A. – **Call toll-free 800-227-4224**
Outside the U.S.A. – **Contact the HACH office or distributor serving you.**
On the Worldwide Web – **www.hach.com**; E-mail – **techhelp@hach.com**

HACH COMPANY
WORLD HEADQUARTERS
Telephone: (970) 669-3050
FAX: (970) 669-2932

Updated April 05 Edition 1